Liquid-Vapor Interface of Ionic Fluids in the Restricted Primitive Model

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The properties of the liquid--vapor interface of ionic fluids in the restricted primitive model (RPM) are investigated within a square-gradient theory. In this comparatively simple theoretical framework, the local free-energy density is expanded in terms of the density gradient and the resulting series is truncated at the square-gradient level. Because of its simplicity, this type of theory is employed very often in calculations of interfacial properties. Here, we compute the density profiles and the interfacial tensions for different temperatures within the "classical" Debye-Hückel (DH) theory and the more recently developed Fisher-Levin (FL) theory, which goes beyond the DH treatment of ion-ion interactions in accounting for ion pairing and the resulting dipole-ion interactions. Since we restrict ourselves to a temperature range of $0.8 \leq T/T_c \leq 0.95$, in which the FL theory is known to give a reasonably accurate description of the coexistence curve of the RPM, the density gradients are small and the employed square-gradient theory is expected to be valid and sufficiently accurate.

Surprisingly, the type of local-density approximation employed in calculating the square-gradient term turns out to be highly relevant for ionic fluids - in sharp contrast to what is found (and known) for simple fluids, such as the square-well fluid or the Lennard-Jones fluid. Depending on the local-density approximation, interfacial thicknesses and tensions may vary by factors of three or four. Guided by the correct low-density behavior of the correlation length, we show which methods can be trusted to yield reliable estimates of the desired interfacial properties.